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Fine and ultrafine TiO₂ particles in aerosol in Kraków (Poland)

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Abstract. During single particle analysis of aerosol in Kraków (Poland) we noticed a new component, that is, aggregates of TiO₂ particles. These aggregates are from 0.5 to 4 μm and are composed of individual particles whose size typically varies from between 100 and 350 nm. Smaller particles (below 100 nm) also occur. TiO₂ particles are relatively abundant in the summer. The size distribution of the particles corresponds to “pigmentary” TiO₂, which indicates that they could be derived from paints and building materials. TiO₂ particles were not previously identified in aerosol samples in Kraków, and therefore this phenomenon is likely to be related to the common usage of new building materials and paints. A review of the literature suggests that TiO₂ particles, especially within the nanosize range, could result in health and environmental impacts; however, evaluation of the actual threat is difficult.

Key-words: TiO₂ particles, single particle analysis, aerosol, Kraków

1. Introduction

We present in this paper the occurrence of TiO₂ fine and ultrafine particles (nanoparticles) in aerosol samples collected in Kraków (Poland). In the summer these particles occur relatively often in the fine fraction of aerosol (< 2.5 μm). Comparison with samples studied in the past (Wilczyńska-Michalik, Michalik 2015 and references therein) indicates that Ti-rich fine particles and nanoparticles (NPs) have become a new and relatively abundant component in aerosols in Kraków.

Natural NPs are ubiquitous in the atmosphere (e.g. sea salt aerosol particles, numerous particles formed during rock weathering or rock disintegration, volcanic eruptions, vegetation fires, particles formed in biological processes or during chemical reactions in the atmosphere). Nanominerals and mineral NPs, their origin, distribution and influence on the Earth system are discussed in numerous papers (e.g. Banfield, Navrotsky 2001; Handy et al. 2008a; Hochella 2008; Hochella et al. 2008; Hawkings et al. 2013).

Anthropogenic NPs are also present in the environment. NPs are emitted into the atmosphere together with more coarse, particulate matter particles during the combustion of fuels (e.g. coal, diesel fuel, biomass). The negative environmental impact and human health threat of fuel combustion products have been extensively studied (e.g. BéruBé et al. 2007). The effect of the instillation of carbon NPs was described by Stoeger et al. (2006). Carbon-rich NPs dominate the emissions from fossil fuel combustion, but other components are also noted, such as nanocrystals of barite in aerosol in the Upper Silesia, Poland (Jabłońska et al. 2003). Part of the dust emitted from numerous industrial installations fulfils the definition of nanomaterials, that is, being composed of particles that are < 100 nm ($0.1 \mu\text{m}$) in at least one dimension. In their review, Kumar et al. (2010) discuss the characteristics of NPs in the urban atmosphere. NPs in the atmospheric environment around traffic routes were studied by Fukuhara et al. (2008).

For approximately three decades it has been possible to observe the increasing rate of production of engineered NPs, that is, intentionally produced particles that have a characteristic dimension of between 1 and 100 nm and exhibit physical and chemical properties different than their non-nanoscale counterparts (Bystrzejewska-Piotrowska et al. 2009; Bernhardt et al. 2010). According to estimates presented by Dawson (2008), nanotechnology was predicted to be involved in the manufacturing processes of more than 15% of all products on the global market by 2014. Nanomaterials could be fixed particles on a substrate or free NPs (Bystrzejewska-Piotrowska et al. 2009). NPs are being incorporated into many products of daily use, such as fillers, opacifiers, catalysts, pharmaceuticals, lubricants, cosmetics, electronic devices, solar cells or other domestic appliances (Bystrzejewska-Piotrowska et al. 2009).

The toxicity of some NPs has been shown, but the mechanisms of influence are poorly studied. Generally, the disadvantageous effect is related to the small size of the NPs, their chemical composition or shape (Bystrzejewska-Piotrowska et al. 2009). Engineered NPs are considered as a novel toxicological challenge (Nowack, Bucheli 2007; Elsaesser, Howard 2012). The list of detailed studies exploring the harmful influence of NPs is long (e.g. Oberdörster et al. 2005; Brayner 2008; Handy et al. 2008b; Navarro et al. 2008; Bottero et al. 2011; Krug 2014). Hu and Gao (2010) present a review of the results of studies on the neurotoxicity of NPs. The broadening range of biomedical applications for NPs results in an emerging need to understand the potential toxicities of these materials (Fadeel, Garcia-Bennett 2010). The interactions of engineered NPs with various molecules in aquatic and soil environments are reviewed by Christian et al. (2008).

The high level concentration of particulate matter (PM) in Kraków is a problem of great concern. PM collected from the atmosphere in Kraków has been studied since the 1970s (Manecki, Wilczyńska 1977). Single particle studies and chemical analyses of PM (Kozak et al. 1998a; 1998b; Wróbel et al. 2000; Worobiec et al. 2006; Samek 2009, Samek 2012; Wilczyńska-Michalik et al. 2010a, 2010b; Wilczyńska-Michalik, Michalik 2015) indicate

that primary and secondary particles are present and that significant seasonal variation of PM composition is visible. The strong domination of very fine and ultrafine particles is observed regardless of the season. Wilczyńska-Michalik and Michalik (2015) present a conclusion on the origin of PM. Primary particles contain mainly natural dust from soil and rock erosion, dust from re-suspension, industrial products, carbonaceous particles from residential coal-based heating, vehicular emissions, and professional power plants. Secondary particles are dominated by sulphates (Ca, Ca-K-Na). The content of secondary organic aerosols has not been evaluated until now.

2. Methods

Dust particles were collected by deposition with meteoric precipitation into glass containers in one month cycles in two sites in the centre of Kraków (two kilometres distance between sites) over a six month period (from January to June 2013). The solutions were filtered through 1.0 μm polycarbonate Nucleopore membrane filters and dried at 60°C. Small amounts of dried sediment were ultrasonically dispersed in water and deposited on 0.2 μm polycarbonate Nucleopore membranes. Fragments of the membranes with deposited dispersed particles were mounted on graphite disc holders and coated with carbon.

The samples were analysed using a Hitachi S-4700 field emission scanning electron microscope (FE-SEM) fitted with a NORAN Nordlys II energy dispersive spectrometer.

3. Results

TiO₂ particles were noticed mostly in samples from the summer; however, it was possible to also note this component in other samples. Rounded particles of TiO₂ occur in the aggregates. The aggregates contain several dozen particles (Fig. 1, 2) or are composed of a smaller number of particles (up to 10) (Fig. 3, 4). The size of aggregates varies from 4 to 0.5 μm in the longest dimension. The diameter of the individual particles varies typically between 100 and 350 nm. Smaller particles (below 100 nm) were rarely observed in the scanning electron microscope images. Taking into account the thickness of the carbon coating layer (ca 20 nm) covering particles, the presence of particles below 100 nm does not raise any doubts.

The content of TiO₂ particles aggregates was approximately determined as a proportion of their number to the total number of particles in the sample (total number of calculated particles was usually from 50 to 60) for the fraction from 2.5 to 0.5 μm . In winter the proportion varied from 0 to 20%. In May values for two sites were 15 and 39%; in June 60 and 73%. Calculated values for 2.5-0.5 μm fraction are much higher than we can expect for PM_{2.5}. It is caused by strong domination of soot nanoparticles in PM_{2.5}.

Ti dominates in the chemical composition of the described particles. Based on the ca 200 of the analyses it is possible to conclude that in most TiO₂ particles, small amounts of Al, Si and occasionally other elements (e.g. Mg) can be detected. Some examples of chemical composition are shown in Table 1. Significant excess of O was measured, compared to the stoichiometric composition of TiO₂. This is caused by a mixing of the

X-ray signal generated inside the TiO_2 particles with the signal from the polycarbonate membrane substratum. The lowest value of atomic O/Ti ratio measured (presented in Table 1) was 1.85. Typically the ratio was above 3, and the highest value obtained was 4.25 (Table 1).

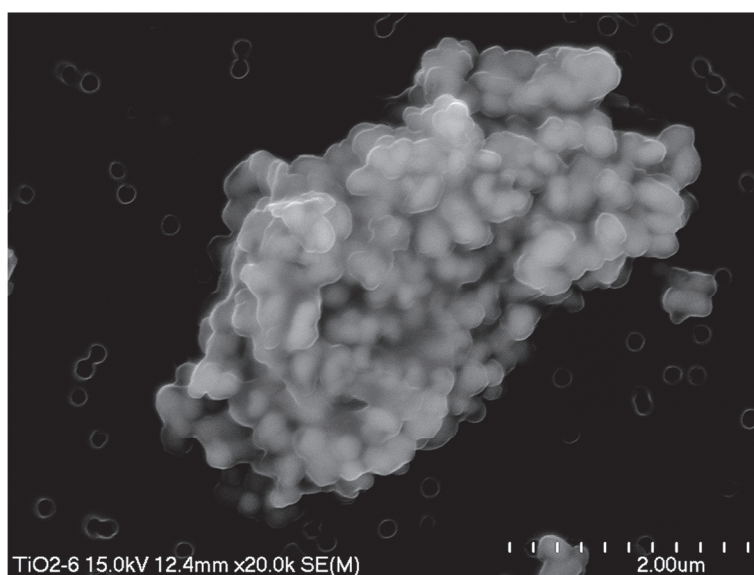


Fig. 1. Aggregate of TiO_2 particles

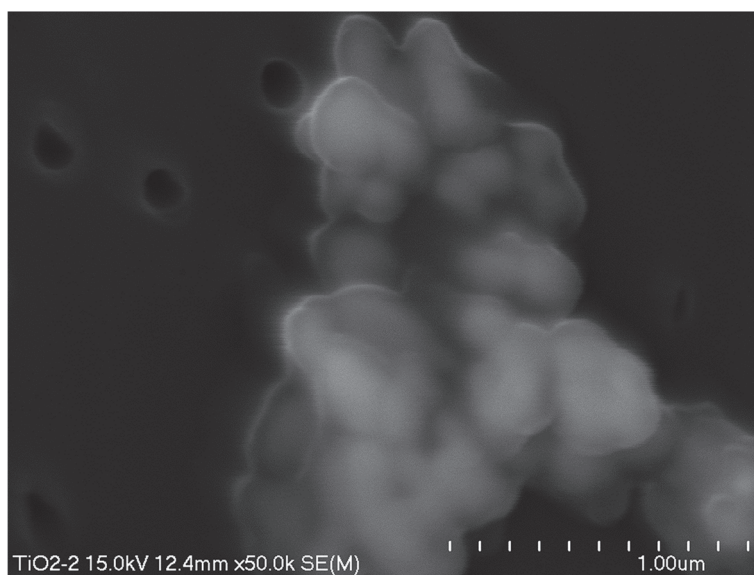


Fig. 2. Aggregate of TiO_2 particles

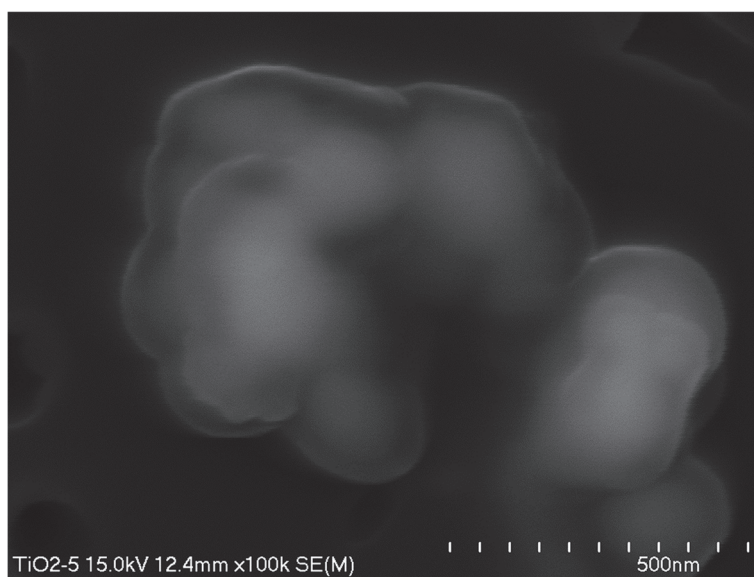


Fig. 3. Aggregate of TiO₂ particles

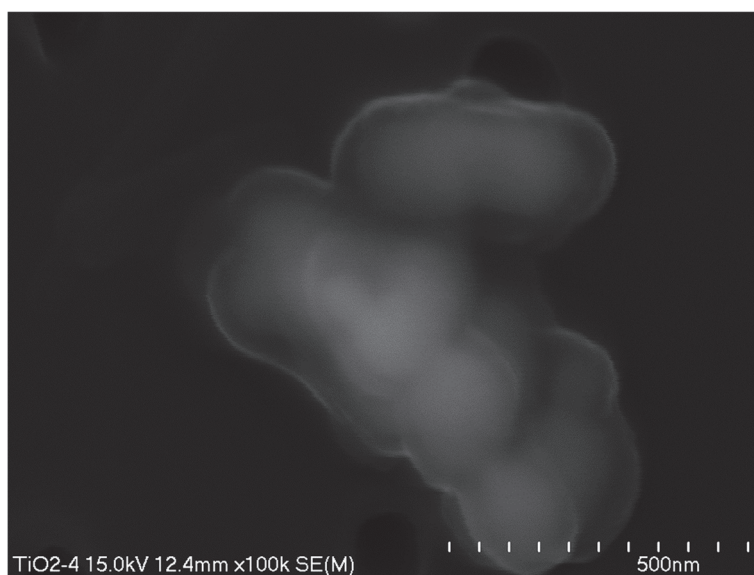


Fig. 4. Aggregate of TiO₂ particles

TABLE 1

Chemical composition of TiO₂ particles (recalculated to oxygen-free basis)

Compound (at. %)	Number of analysis				
	TiO ₂ -2(1)	TiO ₂ -4(1)	TiO ₂ -6(1)	TiO ₂ -8(1)	TiO ₂ -8(6)
Ti	92.01	92.39	94.07	82.02	93.47
Al	6.19	5.19	4.22	3.35	4.20
Si	1.80	2.42	1.71	8.73	2.33
Mg	0.00	0.00	0.00	5.90	0.00
Total	100.00	100.00	100.00	100.00	100.00
O/Ti ratio	3.48	4.25	1.85	3.03	3.85

4. Discussion

4.1. Source of TiO₂ particles

Although Ti is relatively abundant in the lithosphere, the occurrence of TiO₂ particles in atmospheric environments is rarely noted. Jabłońska (2003) describes TiO₂ angular particles (probably rutile), with a rough surface and varying in size from several to several hundred microns, occurring in aerosol samples from the Upper Silesia. The small mineral grains in the aerosol samples could be related to wind erosion of soil or weathered rocks. The common occurrence of relatively uniform in shape, size and chemical composition TiO₂ particles in aerosol in Kraków suggests that their origin is related to industrial processes or emission from widely used industrial products.

Worldwide production of TiO₂ is more than 4.5 million tons and only 4-5% is used to produce metallic Ti (Gázquez et al. 2014). TiO₂ is widely used as a pigment (so called titanium white) because it effectively scatters light almost without absorption of incident light. The scattering is related to reflection from the surface of a crystal, refraction within a crystal, and diffraction (Gázquez et al. 2014). Scattering by diffraction is most effective when the pigment particles' diameter is slightly less than half the wavelength of the light to be scattered (390-700 nm). Because of this, pigment manufacturers tend to maximise the number of TiO₂ particles within the range from ca 200 to 350 nm in their products. It is reasonable to expect that in the material with the maximum situated in this range there are also particles below 100 nm in size (i.e. within the nanoparticle range). This expectation is confirmed by the product descriptions prepared by the manufacturers (e.g. About Titanium Dioxide 2015). Material of this type is used in the production of paints, printing inks, plastics, paper, textiles, ceramics, construction materials, cosmetics, food, and pharmaceuticals, etc. The share of pigmentary form in TiO₂ production is approximately 98%; 1-2% is produced as ultrafine material (About Titanium Dioxide 2014). Ultrafine TiO₂ material (nanomaterial) is used in applications in which transparency and maximum UV light absorption are required (e.g. cosmetic sunscreens). Ultrafine TiO₂ is also used as catalyst supports to remove harmful exhaust gas emissions and in power stations to remove

nitrous oxides (NO_x). The photocatalytic properties of ultrafine TiO₂ are used in the preparation of self-cleaning surfaces. The formation of micrometre-in-size aggregates of TiO₂ NPs is common.

Because of the lack of local TiO₂ manufactures and industrial plants in which TiO₂ is used to prepare TiO₂ containing products in Kraków, the most probable source of TiO₂ particles in particulate matter in the atmosphere could be related to their removal from commonly used products. Taking into account the characteristics of the described TiO₂ particles, it is possible to consider that this material is removed from paints used for building facades or other building materials containing TiO₂ pigment.

The content of Si and Al in studied aggregates of TiO₂ particles could be related to the production technology of some pigments prepared with small admixtures of Si and Al (e.g. Grupa Azoty, Tytanpol 2015).

The rate of erosion of TiO₂ used in paint pigment or as nanocoating on buildings is unknown. According to our knowledge, we do not have data related to the erosion of building facades and the removal of TiO₂ particles into atmospheric or aquatic environments. It is important to also take into account the dispersion of TiO₂ particles during the application of TiO₂ containing materials. Experiments give a general overview of the possible release of TiO₂ particles, but numerous factors are ignored (e.g. the ageing of surfaces, weathering processes, influence of atmospheric pollutants) (e.g. Kaegi et al. 2008; Göhler et al. 2010; Shandilya et al. 2014). Shandilya et al. (2015) showed that surface deterioration of the nanocoated samples was a function of the duration of weathering by ultraviolet light, temperature, and water. The results of Al-Kattan et al.'s (2013) study of artificial weathering indicate that the risk of release of TiO₂ particles into the environment is generally low, but an increase was observed when TiO₂ pigment containing paint was applied on rough surfaces (e.g. on plaster) or after exposure of paint containing nano-TiO₂ to UV-light because of the photocatalytic degradation of the paint matrix.

4.2. Seasonal variation in the abundance of TiO₂ particles in aerosol samples

TiO₂ particles are noted as a common component in summer. This can be caused by two reasons: a higher relative content of TiO₂ particles in aerosol samples, or due to a higher emission rate in this period. During the winter aerosols in Kraków contain numerous carbonaceous particles (soot) which reduce the relative share of other components including TiO₂ particles in aerosols samples. The higher emission rate of TiO₂ particles can be related to the increase in intensity of construction works in the summer, when paints and coating materials containing TiO₂ are used on building facades during construction or renovation. It is worth considering the other possible sources of TiO₂ (e.g. release from textiles; cf. Windler et al. 2012) and the cumulative effect of these emissions.

4.3. Long-term variation in the abundance of TiO₂ particles in aerosol samples

TiO₂ aerosol particles were noted during a single particles study undertaken in Kraków three years ago. During previous studies, material of such chemical composition, morphology and size was not noted in the aerosol samples collected in Kraków (Maneck, 2012).

Wilczyńska 1977; Kozak 1998a, 1998b; Wilczyńska-Michalik et al. 2010a, 2010b). Therefore, it can be considered as a new component in particulate matter in the atmosphere of Kraków related to significant market introduction of various new building materials, mostly paints.

4.4. Potential environmental and health impact of TiO₂ particles

The occurrence of a new type of atmospheric PM component in Kraków indicates the need for consideration of its possible environmental and human health impacts. Jabłońska (2013) described TiO₂ particles in human lung tissues. The presence of TiO₂ PM also indicates the possibility of their accumulation in soil and aquatic environments. It is commonly accepted that the influence of pigmentary TiO₂ (i.e. non-nanosize) on human health is inert, which partly agrees with general opinion that NPs are always more toxic than micrometre particles of the same chemical composition (e.g. Wang et al. 2005). The negative effect of TiO₂ NPs in sunscreens and cosmetics was studied by Tucci et al. (2013). Shukla et al. (2013) present results showing that TiO₂ NPs induce DNA damage and cause apoptosis in human liver cells, even at very low concentrations. Dunford et al. (1997) studied the role of TiO₂ used in sunscreens in aquatic environments. TiO₂ catalyses photo-oxidation of organic substrate and causes oxidative damage to DNA *in vitro* and in human cells. Also, degradation of NPs containing TiO₂ in the core can result in TiO₂ exposition, which leads to unwanted effects (e.g. photo-oxidation reaction or generation of reactive oxygen species) (Auffan et al. 2010). The health effect of TiO₂ NPs was studied by numerous authors (e.g. Chen et al. 2012; Chang et al. 2013). TiO₂ NPs produce reactive oxygen species which results in their neurotoxicity (Long et al. 2006). Geiser et al. (2014) studied the effects of inhaled TiO₂ NPs in potential mechanisms for the increased susceptibility of cystic fibrosis patients to air pollution. Grassian et al. (2007) show an inflammatory response to the inhalation of TiO₂ NPs of a primary size of 2 to 5 nm. Some studies suggest that the interactions of TiO₂ NPs with other chemicals may result in an increase in toxicity (Liu et al. 2013).

Karlsson et al. (2009) present a different opinion, however, indicating that the micrometre particles of TiO₂ cause more DNA damage compared to the TiO₂ NPs. They suggest that the toxicity of TiO₂ particles is strongly related to their structure (rutile or anatase) and surface properties. Warheit (2004) concludes that exposure to uncoated TiO₂ NPs (~ 50 nm) does not enhance lung inflammation in rats in comparison with larger TiO₂ particles (~ 300 nm). Warheit (2004) also indicates that different surface coatings on particles can influence differences in pulmonary inflammation.

The possible impact of TiO₂ NPs is actively studied, but it is difficult to assess real hazards. The problem is important because it is assumed that the annual production of TiO₂ NPs will reach 2.5 million tons by 2025 (Robichaud et al. 2009 in Dwivedi, Ma 2014).

Chen et al. (2014) studied the interaction of TiO₂ NPs with humic acids in order to explain the impact of these NPs on natural organic matter in aquatic environments. Hu et al. (2011) describe the role of TiO₂ NPs in Cd accumulation in Zebrafish in humic acid solution. The decrease in Caribbean reef-building coral populations caused by stress induced by nano-TiO₂ was studied by Jovanović and Guzmán (2014). Based on the study of toxicity of nanosize TiO₂ aggregates in marine environment, Zhu et al. (2011) conclude that

both a direct and indirect effect on abalone embryonic development occurs. TiO₂ NPs are phototoxic to marine phytoplankton (Miller et al. 2012). TiO₂ NPs influence the growth and metabolism of algae (Cardinale et al. 2012).

Du et al. (2011) studied the role of TiO₂ and ZnO NPs in soil environments and showed a negative influence on wheat growth. Ge et al. (2011) discuss the negative effects of TiO₂ and ZnO NPs on soil bacterial communities. TiO₂ appears to affect earthworm reproductive activity (Schlich et al. 2012).

4.5. Changes in composition of aerosol samples

The development of new technologies, emergence of new industrial branches, and common application of new devices could result in the emission of new pollutants (e.g. nanowastes; see Bystrzejewska-Piotrowska et al. 2009) of unknown environmental and health impacts. Detail studies of aerosol particles offer the possibility for monitoring their composition and the occurrence of new components.

5. Conclusions

- 1) Fine and ultrafine particles of TiO₂ occur in atmospheric particulate matter in Kraków. The size distribution of these particles indicates that they correspond to “pigmentary” TiO₂, and thus they could be derived from paints and building materials.
- 2) Abundance is higher in summer, which is probably related to the high intensity of construction works in Kraków at this time.
- 3) TiO₂ particles currently occur in aerosol samples relatively common but their presence has not been noted in the past. This is probably related to the common usage of new building materials and paints.
- 4) A review of the available literature indicates that TiO₂ particles, especially within the nanosize range, could result in health and environmental impacts; however, any evaluation of the actual threat is difficult.
- 5) Studies of aerosol particles’ composition and abundance together with their accumulation in soil and aquatic environments are needed for the identification of new pollutants and evaluation of their potential hazards.

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